The Second Law of Thermodynamics

The second law of thermodynamics asserts that processes occur in a certain direction and that the energy has *quality* as well as *quantity*.

The first law places no restriction on the direction of a process, and satisfying the first law does not guarantee that the process will occur. Thus, we need another general principle (second law) to identify whether a process can occur or not.

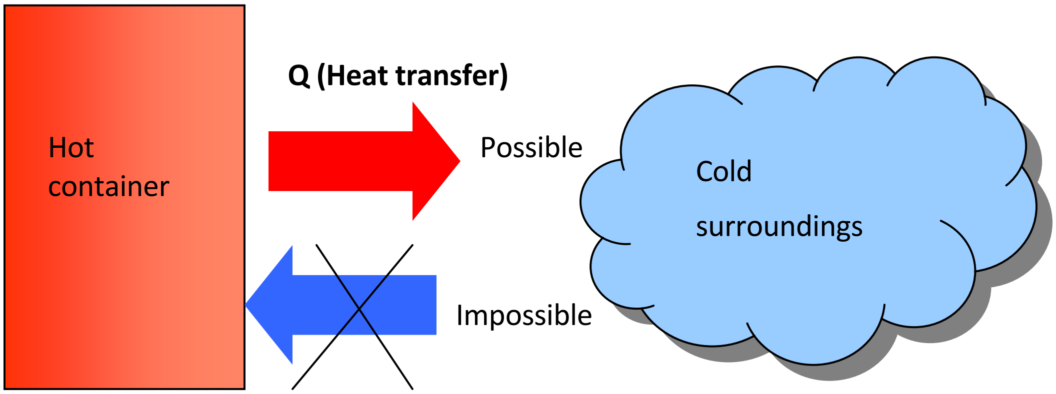


Fig. 1: Heat transfer from a hot container to the cold surroundings is possible; however, the reveres process (although satisfying the first law) is impossible.

A process can occur when and only when it satisfies both the first and the second laws of thermodynamics.

The second law also asserts that energy has a quality. Preserving the quality of energy is a major concern of engineers. In the above example, the energy stored in a hot container (higher temperature) has higher quality (ability to work) in comparison with the energy contained (at lower temperature) in the surroundings.

The second law is also used in determining the theoretical limits for the performance of commonly used engineering systems, such as heat engines and refrigerators etc.

Thermal Energy Reservoirs

Thermal energy reservoirs are hypothetical bodies with a *relatively* large thermal energy capacity (mass x specific heat) that can supply or absorb finite amounts of heat *without undergoing any change in temperature*. Lakes, rivers, atmosphere, oceans are example of thermal reservoirs.

A two-phase system can be modeled as a reservoir since it can absorb and release large quantities of heat while remaining at constant temperature.

A reservoir that supplies energy in the form of heat is called a *source* and one that absorbs energy in the form of heat is called a *sink*.

Heat Engines

Heat engines convert heat to work. There are several types of heat engines, but they are characterized by the following:

1- They all receive heat from a high-temperature source (oil furnace, nuclear reactor, etc.)

2- They convert part of this heat to work

3- They reject the remaining waste heat to a low-temperature sink

4- They operate in a cycle.

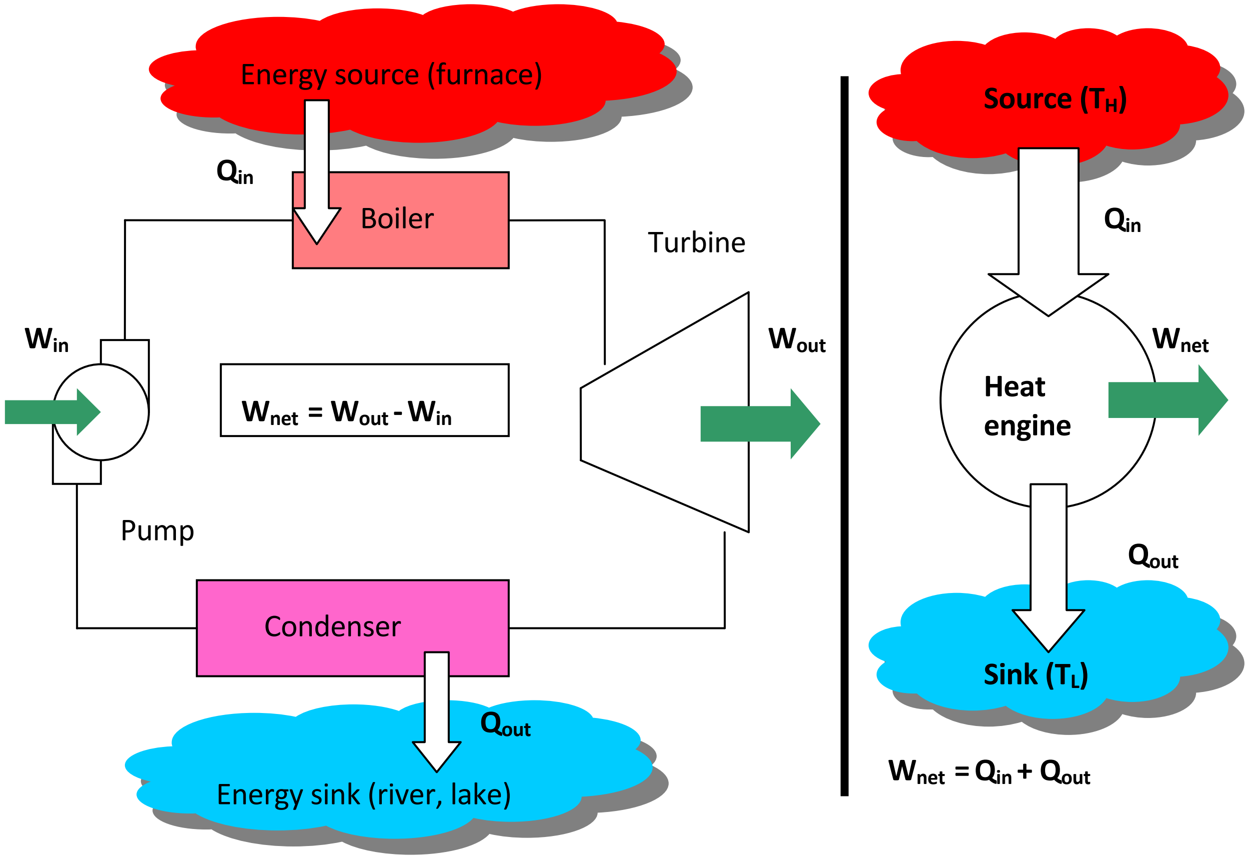


Fig. 2: Steam power plant is a heat engine.

Thermal efficiency: is the fraction of the heat input that is converted to the net work output (efficiency = benefit / cost).

$$\eta_{th} = \frac{W_{net,out}}{Q_{in}} \qquad and \qquad W_{net,out} = Q_{in} - Q_{out}$$

$$\eta_{th} = 1 - \frac{Q_{out}}{Q_{in}}$$

The thermal efficiencies of work-producing devices are low. Ordinary spark-ignition automobile engines have a thermal efficiency of about 20%, diesel engines about 30%, and power plants in the order of 40%.

Is it possible to save the rejected heat Q_{out} in a power cycle? The answer is NO, because without the cooling in condenser the cycle cannot be completed. Every heat engine *must* waste some energy by transferring it to a *low-temperature* reservoir in order to complete the cycle, *even in idealized cycle*.

The Second Law: Kelvin-Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work. In other words, no heat engine can have a thermal efficiency of 100%.

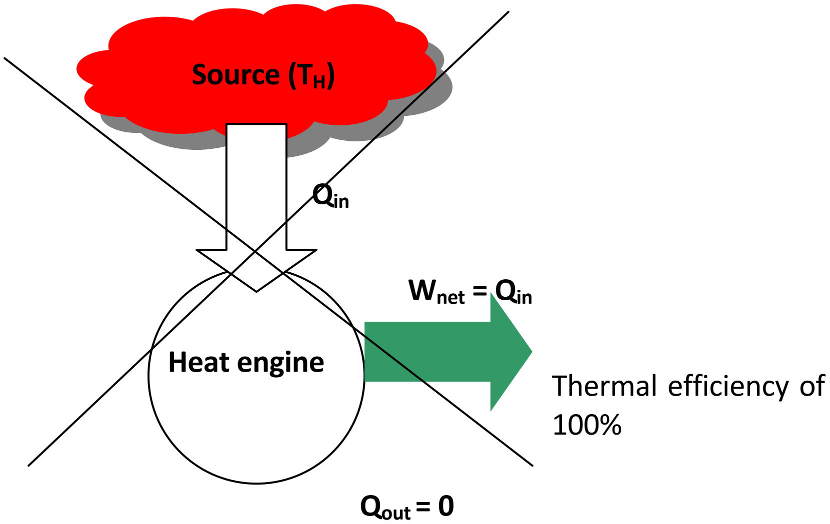
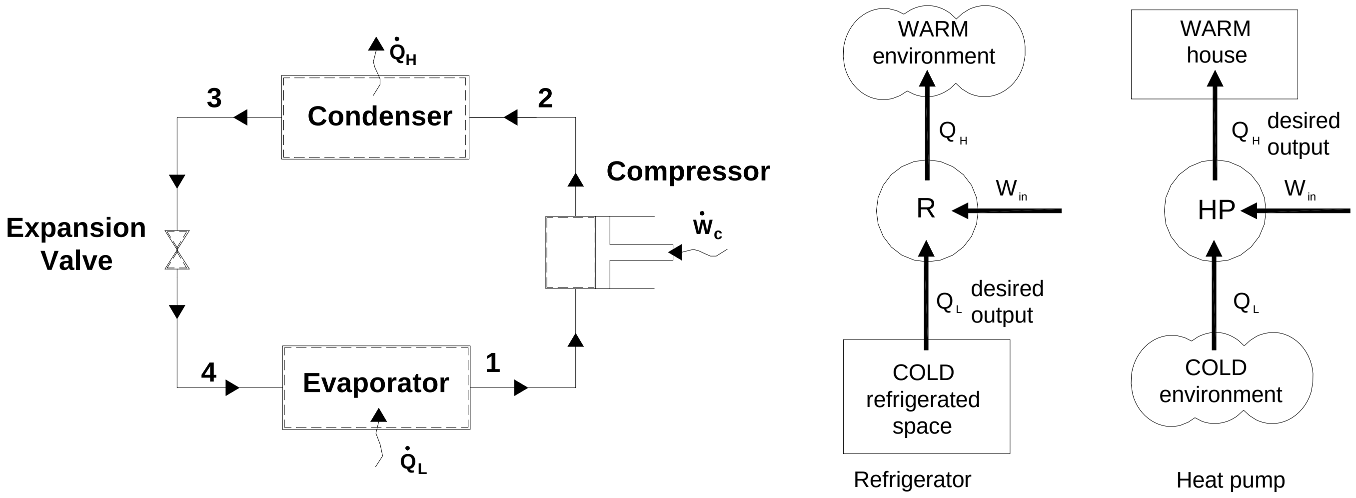


Fig.3: A heat engine that violates the Kelvin-Planck statement of the second law cannot be built.

Refrigerators and Heat Pumps

In nature, heat flows from high-temperature regions to low-temperature ones. The reverse process, however, cannot occur by itself. The transfer of heat from a low-temperature region to a high-temperature one requires special devices called *refrigerators*. Refrigerators are cyclic devices, and the working fluids used in the cycles are called *refrigerant*.

Heat pumps transfer heat from a low-temperature medium to a high-temperature one. Refrigerators and heat pumps are essentially the same devices; they differ in their objectives only. Refrigerator is to maintain the refrigerated space at a low temperature. On the other hand, a heat pump absorbs heat from a low-temperature source and supplies the heat to a warmer medium.



Refrigerator

Heat pump

Fig. 4: Objectives of refrigerator and heat pump.

Coefficient of Performance (COP)

The performance of refrigerators and heat pumps is expressed in terms of the coefficient of performance (COP) which is defined as

$$COP_R = \frac{Benefit}{Cost} = \frac{q_L}{w_c} \qquad COP_{HP} = \frac{Benefit}{Cost} = \frac{q_H}{w_c}$$

It can be seen that

$$COP_{HP} = COP_R + 1$$

Air conditioners are basically refrigerators whose refrigerated space is a room or a building.

The Energy Efficiency Rating (EER): is the amount of heat removed from the cooled space in BTU's for 1 Wh (watt-hour)

$$\text{EER} = 3.412\ \text{COP}_R$$

Most air conditioners have an EER between 8 to 12 (COP of 2.3 to 3.5).

The Second Law of Thermodynamics: Clausius Statement

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to higher-temperature body. In other words, a refrigerator will not operate unless its compressor is driven by an external power source.

Kelvin-Planck and Clausius statements of the second law are negative statements, and a negative statement cannot be proved. So, the second law, like the first law, is based on experimental observations.

The two statements of the second law are equivalent. In other words, any device violates the Kelvin-Planck statement also violates the Clausius statement and vice versa.

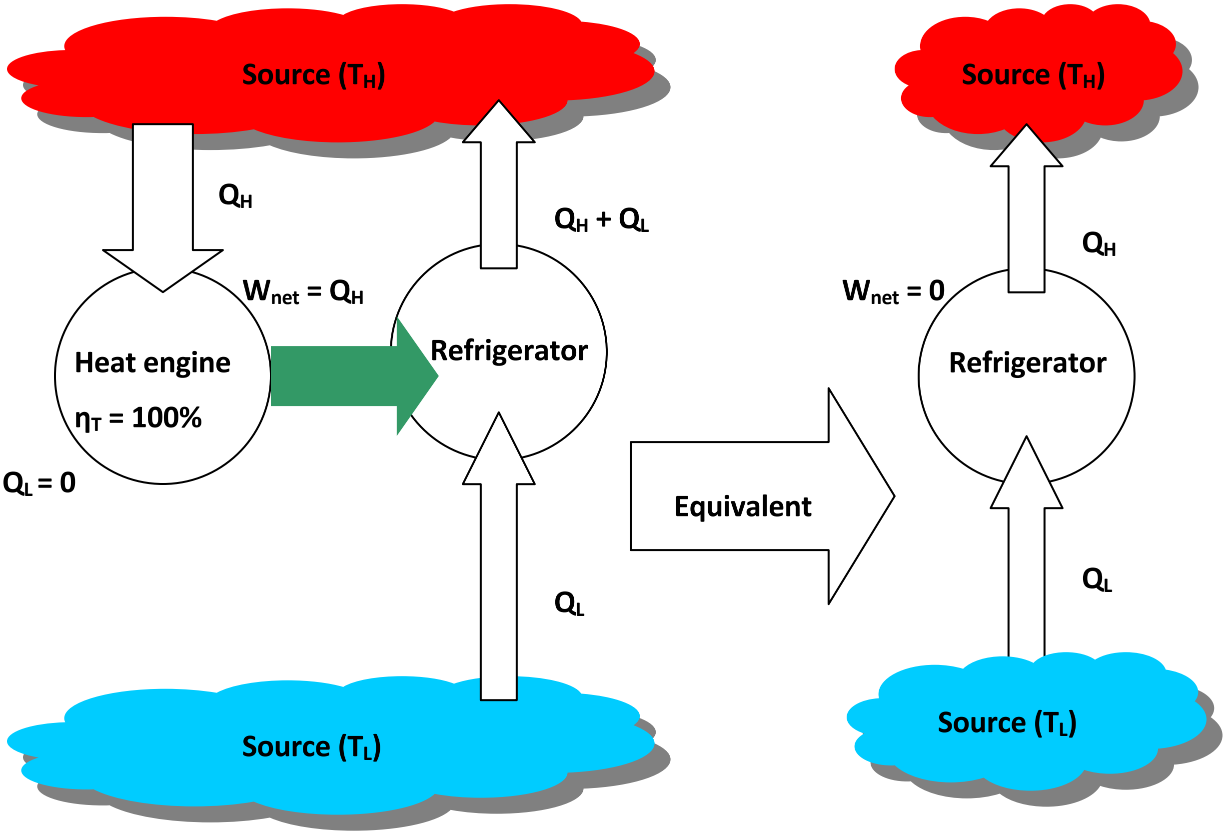


Fig. 5: The violation of the Kelvin-Planck statement leads to violation of Clausius.

Any device that violates the first law of thermodynamics (by creating energy) is called a *perpetual-motion machine of the first kind* (PMM1), and the device that violates the second law is called a *perpetual-motion machine of the second kind* (PMM2).

Reversible and Irreversible Process

A *reversible* process is defined as a process that can be reversed without leaving any trace on the surroundings. It means both system and surroundings are returned to their initial states at the end of the reverse process. Processes that are not reversible are called *irreversible*.

Reversible processes do not occur and they are only idealizations of actual processes. We use reversible process concept because, a) they are easy to analyze (since system passes through a series of equilibrium states); b) they serve as limits (idealized models) to which the actual processes can be compared.

Some factors that cause a process to become irreversible:

- Friction
- Unrestrained expansion and compression

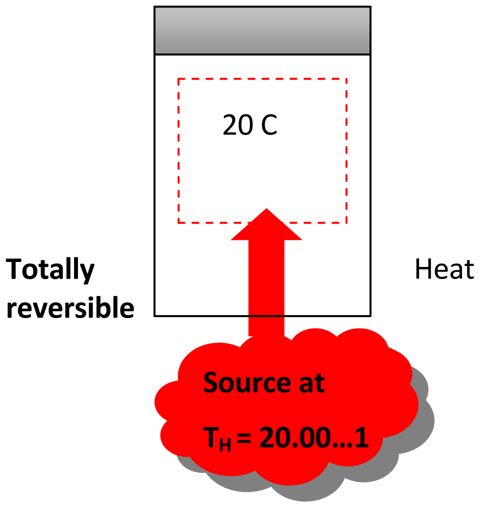
- mixing
- Heat transfer (finite ΔT)
- Inelastic deformation
- Chemical reactions

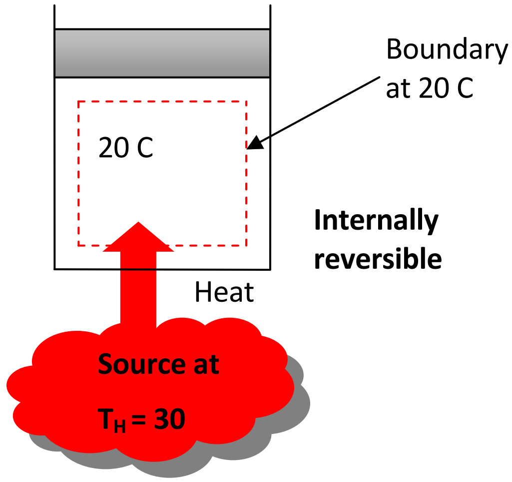
In a reversible process things happen very slowly, without any resisting force, without any space limitation → everything happens in a highly organized way (it is not physically possible - it is an idealization).

Internally reversible process: if no irreversibilities occur within the boundaries of the system. In these processes a system undergoes through a series of equilibrium states, and when the process is reversed, the system passes through exactly the same equilibrium states while returning to its initial state.

Externally reversible process: if no irreversibilities occur outside the system boundaries during the process. Heat transfer between a reservoir and a system is an externally reversible process if the surface of contact between the system and reservoir is at the same temperature.

Totally reversible (reversible): both externally and internally reversible processes.





The Carnot Cycle

The efficiency of a heat-engine cycle greatly depends on how the individual processes that make up the cycle are executed. The net work (or efficiency) can be maximized by using reversible processes. The best known reversible cycle is the *Carnot cycle*.

Note that the reversible cycles cannot be achieved in practice because of irreversibilities associated with real processes. But, the reversible cycles provide upper limits on the performance of real cycles.

Consider a gas in a cylinder-piston (closed system). The Carnot cycle has four processes:

1-2 Reversible isothermal expansion: The gas expands slowly, doing work on the surroundings. Reversible heat transfer from the heat source at T_H to the gas which is also at T_H.

2-3 Reversible adiabatic expansion: The cylinder-piston is now insulated (adiabatic) and gas continues to expand reversibly (slowly). So, the gas is doing work on the surroundings, and as a result of expansion the gas temperature reduces from T_H to T_L.

3-4: Reversible isothermal compression: The gas is allowed to exchange heat with a sink at temperature T_L as the gas is being slowly compressed. So, the surroundings is doing work (reversibly) on the system and heat is transferred from the system to the surroundings (reversibly) such that the gas temperature remains constant at T_L.

4-1: Reversible adiabatic compression: The gas temperature is increasing from T_L to T_H as a result of compression.

Carnot cycle is the most efficient cycle operating between two specified temperature limits.

The efficiency of all reversible heat engines operating between the two same reservoirs are the same.

The thermal efficiency of a heat engine (reversible or irreversible) is:

$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

For the Carnot cycle, it can be shown:

$$\eta_{th,Carnot} = 1 - \frac{T_L}{T_H}$$

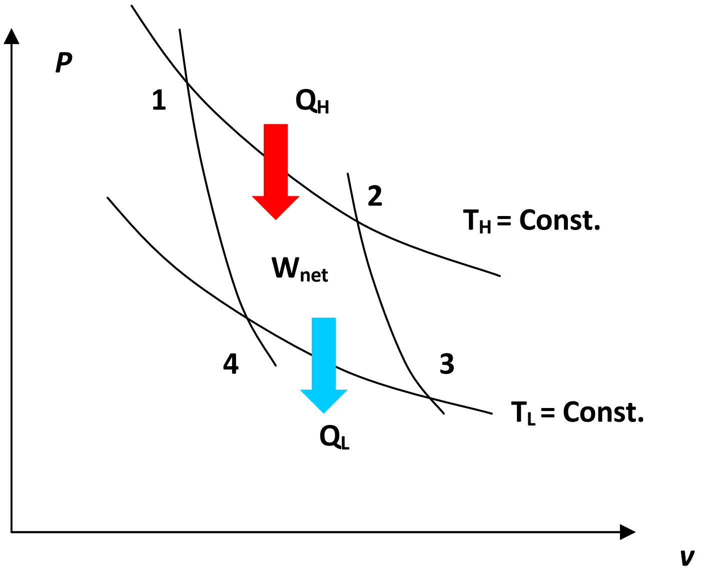


Fig. 6: P-v diagram for the Carnot cycle.

The efficiency of an irreversible (real) cycle is always less than the efficiency of the Carnot cycle operating between the same two reservoirs.

$$\eta_{th} = \begin{cases} < \eta_{th,rev} & \text{irreversible heat engine} \\ = \eta_{th,rev} & \text{reversible heat engine} \\ > \eta_{th,rev} & \text{impossible heat engine!} \end{cases}$$

Consider a Carnot heat engine working between two thermal reservoirs T_L = 300 K and T_H. The thermal efficiency of the heat engine increases as the heat source temperature T_H is increased.

T_H K	**η_{th} %**
1000	70
900	66.6
500	40
350	14.3

The thermal efficiency of actual heat engine can be maximized by supplying heat to the engine at the highest possible temperature (limited by material strength) and rejecting heat to lowest possible temperature (limited by the cooling medium temperature such as atmosphere, lake, river temperature).

From the above table, it can also be seen that the energy has a quality. More of the high-temperature thermal energy can be converted to work. Therefore, the higher the temperature, the higher the quality of the energy will be.

The Carnot Refrigeration and Heat Pump Cycle

A refrigerator or heat pump that operates on the reverse Carnot cycle is called a *Carnot Refrigerator*, or a *Carnot heat pump*.

The Coefficient of performance of any refrigerator or heat pump (reversible or irreversible) is given by:

$$COP_R = \frac{1}{Q_H / Q_L - 1} \quad \text{and} \quad COP_{HP} = \frac{1}{1 - Q_L / Q_H}$$

COP of all reversible refrigerators or heat pumps can be determined from:

$$COP_{R,rev} = \frac{1}{T_H / T_L - 1} \quad \text{and} \quad COP_{HP,rev} = \frac{1}{1 - T_L / T_H}$$

Also, similar to heat engine, one can conclude:

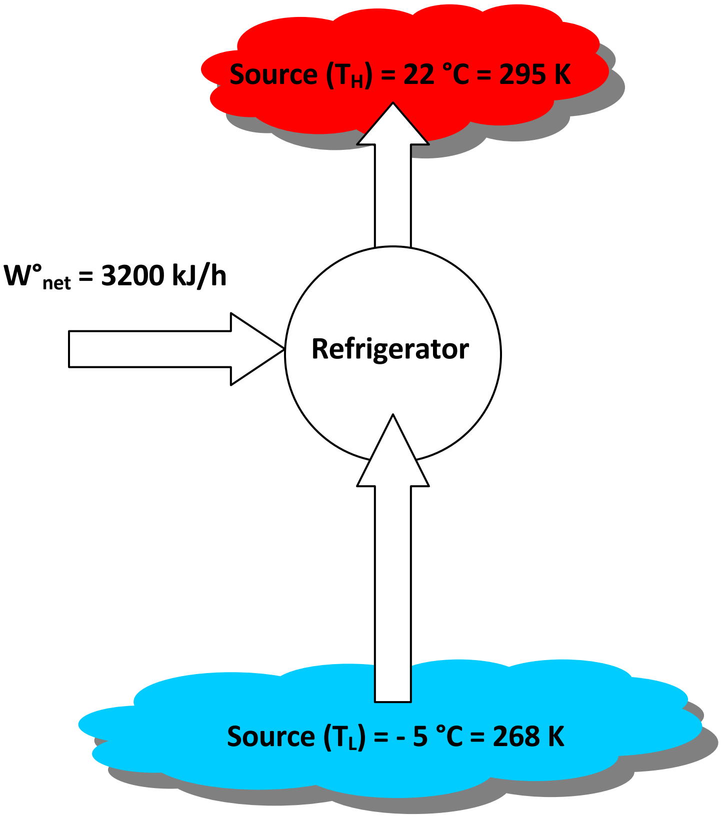
$$COP_R = \begin{cases} < COP_{R,rev} & \text{irreversible refrigerator} \\ = COP_{th,rev} & \text{reversible refrigerator} \\ > COP_{th,rev} & \text{impossible refrigerator!} \end{cases}$$

Example 1: Refrigerator Performance

A refrigerator maintains the temperature of the freezer compartment at -5 C when the air surrounding the refrigerator is at 22 °C. The rate of heat transfer from the freezer compartment to the refrigerant (the working fluid) is 8000 kJ/h and the power input required to operate the refrigerator is 3200 kJ/h. Determine the coefficient of performance of the refrigerator and compare with the coefficient of performance of a reversible refrigeration cycle operating between reservoirs at the same temperatures.

Assumptions:

- Steady-state operation of the refrigerator.
- The freezer compartment and the surrounding air play the roles of the cold and hot reservoirs, respectively.



The coefficient of performance of the refrigerator is:

$$\mathrm{COP_R} = \dot{Q}_C / \dot{W}_{cycle}$$

$$\mathrm{COP_R} = 8000\ \mathrm{(kJ/h)} / 3200\ \mathrm{(kJ/h)} = 2.5$$

The coefficient of performance of a Carnot refrigerator working between the same two reservoirs is:

$$COP_{R,Carnot} = \frac{1}{T_H / T_C - 1} = \frac{1}{295/268 - 1} = 9.9$$